

# SCIENCE FOR CERAMICS PRODUCTION

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## SYNTHESIS OF PIGMENTS FOR BULK COLORING FROM REFRACTORY CLAY

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The results of a study of the possibility of bulk coloring of tile pastes by impregnating the clay with solution of salts of 3d-elements (Ni, Co, Cr, Fe), which allows obtaining pigments of mullite-like structure with high chromophoric indexes based on energy-saving technology, are reported. The use of natural raw material and soluble salts of 3d-elements makes it possible to significantly expand the raw-material base, reduce the cost of the manufactured product by replacing expensive materials and combining synthesis of pigments and firing of the articles.

Different natural silicates, including laminar silicates such as refractory clays, are used in synthesis of ceramic pigments [1]. Kaolinite  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  is the basic rock-forming mineral. The crystal lattice of kaolinite, a mineral of lamellar structure, is of the open packing type, consisting of two layers: octahedral and tetrahedral. The first consists of silicon-oxygen tetrahedrons  $[\text{SiO}_4]^{4-}$  and the second consists of aluminum cations. Hydroxyl ions  $[\text{OH}]^-$  are positioned on one side of the packing. Tetrahedral layers are shifted by 1/3 with respect to the octahedral layers.

LT-1 clay from the Latnensk deposit was used as the initial feedstock. This clay is refractory, finely disperse, high-temperature sintering, and contains no more than 2.5% coloring oxides ( $\text{Fe}_2\text{O}_3 + \text{TiO}_2$ ).<sup>2</sup>

In selecting the basic raw materials, we were guided by the properties of the clays, which allow isomorphic substitution of  $\text{Al}^{3+}$  ions of transition 3d-elements ( $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ). The good wettability of the clays makes it possible to rapidly impregnate the clays with solutions of salts of the coloring ions of transition 3d-elements. Preliminary impregnation of the clays allows combining firing of the ceramic ware and synthesizing pigments, which reduces heat and power consumption in production of ceramic materials.

We investigated the features of coloring of ceramic materials with synthetic pigments and impregnation with the salts of transition d-elements and the possibility of incorporating

coloring ions in the crystal structure of a natural mineral — refractory clay, without additional charge adjustment.  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Ni}^{2+}$  ions were used as chromophores [2, 3].

The pigment paste colored with the solutions of transition metal salts was obtained as follows. LT-1 clay was dried, ground, sieved, then impregnated with 35% solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Co}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$  in the amount of 5, 10, and 15% in terms of oxides. A solution of acetic acid (3 ml of 9%  $\text{CH}_3\text{COOH}$  per 100 ml of salt solution) was added to increase the porosity of the clay and ensure better impregnation. Hot solutions ( $80 \pm 10^\circ\text{C}$ ) were used for better dissolution of the salts and more careful coloring of the clay raw material. The mineralizer was 5% borax  $\text{H}_3\text{BO}_3$ . For comparing the chromophoric properties of the salts and oxides of the same metals, LT-1 clay was also colored with oxides —  $\text{CoO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{NiO}$ .

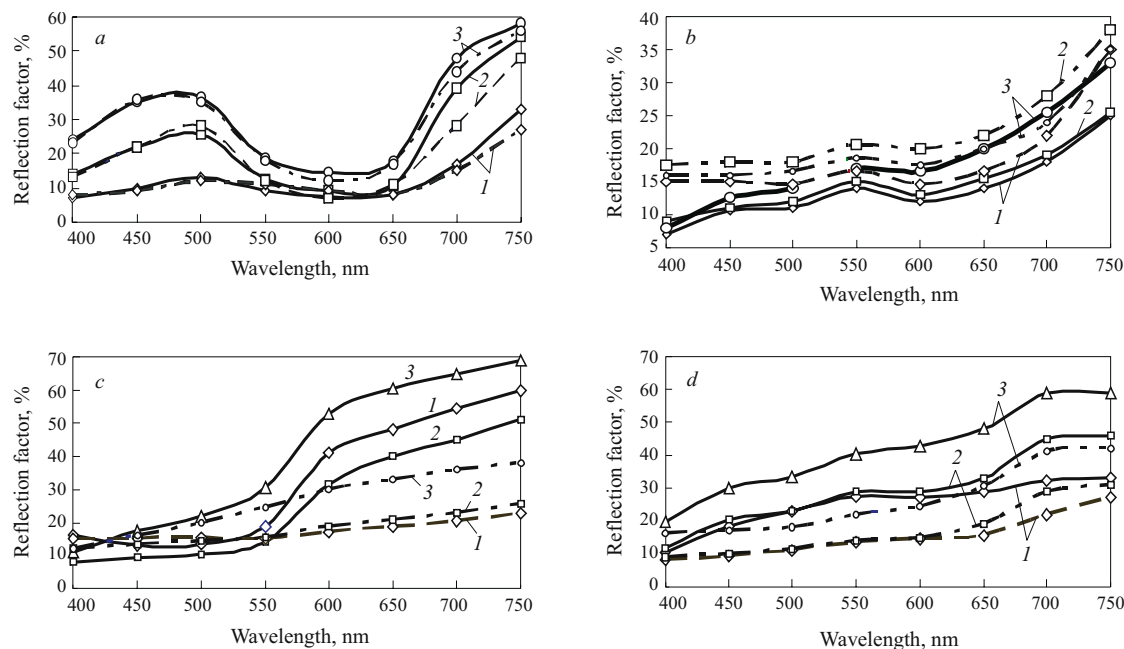
The colored clay was fired in an electric furnace at  $1100 - 1150 - 1200 \pm 20^\circ\text{C}$  with holding at the maximum temperature for 1 h. Pigments of different colors and hues were obtained as a result of high-temperature treatment of the colored pastes.

The change in the spectral properties of the pigments synthesized with transition metal salts and oxides was also investigated. The spectral reflection curves of the pigments are shown in Fig. 1.

The reflection spectrum coefficients increased in the 470 – 500 nm region for the synthesized cobalt-containing pigments, corresponding to dark-light blue color. The pig-

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<sup>2</sup> Here and below: mass content.



**Fig. 1.** Spectral reflection curves of pigments — cobalt-containing (a), chromium-containing (b), iron-containing (c), and nickel-containing (d): 1, 2, and 3) pigments with 5, 10, and 15% oxide content added in the form of a solution of salts (solid curves) and oxides (dashed curves).

ments colored with salts and oxides had the same amount of chromophores, but their spectral characteristics were different, which indicates more intensive coloring of the pigments by salts in comparison to oxides.

The spectral reflection curves of the chromium-containing pigments had the dominant wavelength in the 500 – 530 nm region, which corresponds to the green region of the spectrum. The pigments obtained by coloring with chromium ions also produced bright and saturated coloring. Use of the salts allows obtaining pigments with 3 – 8% higher purity of hue than with the previously synthesized pigment.

The coloring of iron-containing pigments synthesized with oxides was characterized by the light brown scale, and the absorption maximum was in the 580 – 590 nm region.

The pigments synthesized with solutions of salts were distinguished by more saturated brown coloring and the dominant wavelength in the 590 – 610 nm region.

Nickel-containing pigments had reflection curves with a central absorption band in the 550 nm region. The color of the pigments varied from green to dark green. This change in the color of the pigments was due to the presence of the  $[\text{NiO}_6]$  octahedral complex, for which three absorption maxima in different regions of the spectrum are characteristic.

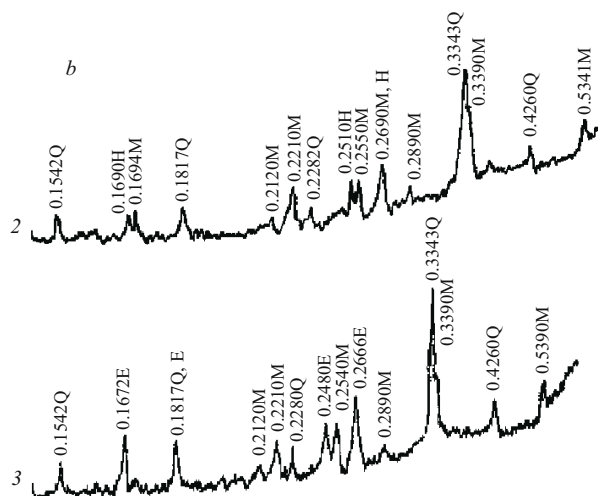
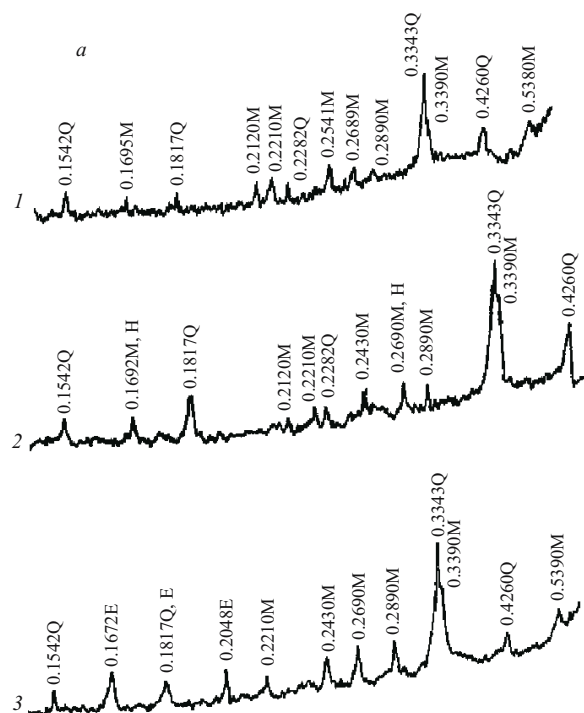
The color characteristics of pigments synthesized with use of oxides and salts are reported in Table 1.

The mechanisms and features of synthesis of pigments using transition metal oxides and salts as chromophores were investigated. It was found that the chromophoric properties of the salts were manifested to a greater degree than with the oxides. Synthesis of pigments by the salt impregnation method produces more intensely colored pigments due to the ability of 3d-element salts to more uniformly color the clay by penetrating into microcracks in the grains and being adsorbed on their surfaces. The pigments made with salts had a purity of hue 3 – 15% higher than the pigments containing a similar amount of 3d-element oxides in the paste.

When the chromophore content was increased from 5 to 15%, the color of the pigments changed, producing different shades of the same color. When the amount of added chromophore was decreased by 5%, the purity of hue decreased by 5 – 15%, and the dominant wavelength was shifted to the region of longer waves. The use of  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Fe}^{3+}$  as coloring ions made it possible to synthesize the brightest pigments with high purity of hue.

**TABLE 1**

Type of 3d-element	Color index coordinates		Dominant wavelength, nm	Purity of hue, %
	<i>X</i>	<i>Y</i>		
<i>Pigments synthesized with oxides</i>				
CoO	0.134	0.258	485	68
Cr <sub>2</sub> O <sub>3</sub>	0.211	0.551	515	67
Fe <sub>2</sub> O <sub>3</sub>	0.413	0.386	590	52
NiO	0.320	0.433	550	50
<i>Pigments synthesized with solutions of salts</i>				
Co <sup>2+</sup>	0.129	0.197	480	70
Cr <sup>3+</sup>	0.243	0.573	530	75
Fe <sup>3+</sup>	0.523	0.349	610	69
Ni <sup>2+</sup>	0.311	0.479	550	60



**Fig. 2.** X-ray patterns ( $d$ , nm) of pigments based on transition 3d-element oxides (a) and salts (b): 1) fired clay; 2 and 3) iron- and chromium-containing pigments, respectively; Q) quartz; M) mullite; H) hematite; E) eskolaite.

The studies showed that synthesis of pigments based on refractory clay is economically better in comparison to pure oxides. The presence of alkaline-earth metals in the clay decreased the sintering temperature and eliminated use of mineralizers. The pigments based on refractory clay were synthesized at 1150–1200°C with holding for 1 h, which is 100–150°C lower than the synthesis temperature for pigments using the pure oxides.

The phase composition of the pigments obtained was investigated by x-ray phase analysis. It was found that the structure of the clay is rearranged with formation of the crystal lattice of mullite. The phase composition of the pigments (Fig. 2) is basically represented by  $\alpha$ -quartz, a solid solution of mullite, and coloring chromium and iron oxides in the form of an independent phase.

$\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  ionic chromophores are hypothetically incorporated in the mullite crystal lattice in the pigments colored with the salt solutions (reflections at 0.1694, 0.2550, and 0.2690 nm). This is due to the close values of the ion radii of  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  to the radius of  $\text{Al}^{3+}$  in the crystal lattice of mullite and results in stable pigments with optimum chromophoric properties. The limited volume of the mullite crystal lattice was found and confirmed by the presence of coloring chromium and iron oxides in the form of independent phases. This shows that it is better to synthesize pigments with solutions of salts to obtain pigments of mullite-like structure which are more resistant to high temperatures.

The possibility of using pigments of these compositions for coloring tile pastes with partial substitution of the clay by paste colored with 3d-element salts was investigated.

In bulk coloring of tile pastes, positive results were obtained in using pigments containing  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Fe}^{3+}$  ions. The pigments containing  $\text{Ni}^{2+}$  ions did not give the articles bright coloring, but they can be used as shading colors. It should be noted that almost the same effect is obtained in coloring the samples by incorporation of fired and unfired pigment.

The effect of the synthesized pigments and colored clay powders on the physicochemical properties of the tiles was established. The analysis of the basic physicochemical properties of the synthesized samples indicates the absence of any negative effect of the pigment on the properties of the articles. The physicochemical characteristics of the samples correspond to GOST 6787.

It is thus expedient to use the method of impregnating the clay with solutions of salts of 3d-elements (Ni, Co, Cr, Fe) for bulk-colored pastes as pigments with a mullite-like structure with high chromophoric indexes can be obtained with energy-saving technology. The use of natural raw materials and soluble 3d-element salts will make it possible to expand the raw material base, reduce the cost of the finished product by replacing expensive materials, and combining synthesis of the pigments and firing of the articles.

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